



# (12) UK Patent Application (19) GB (11) 2 003 891 A

- (21) Application No: 7834454  
(22) Date of filing:  
24 AUG 1978  
(23) Claims filed:  
24 AUG 1978  
(30) Priority data:  
(31) 833360  
(32) 14 SEP 1977  
(33) UNITED STATES OF AMERICA (US)  
(43) Application published:  
21 MAR 1979  
(51) INT. CL.<sup>2</sup>: C08L 25/06  
(C08L 25/06 23/02 53/02)  
(52) Domestic classification:  
C3M 127AC 139 140 143  
143A 146 146A 202 L  
(56) Documents cited:  
GB 1328446  
(58) Field of search:  
C3M  
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(54) COMPOSITION OF A POLYSTYRENE RESIN, AND A PRECOMPOUNDED POLYMER SYSTEM COMPRISING A POLYOLEFIN AND A SELECTIVELY HYDROGENATED BLOCK COPOLYMER OF A VINYL AROMATIC COMPOUND AND AN OLEFINIC ELASTOMER

(57) There are provided compositions comprising (a) a polystyrene resin; and (b) a precompounded polymer system comprising an olefinic resin and a selectively hydrogenated elastomeric block copolymer resin alone, or in further combination with a polystyrene resin; and (c) optionally, a hydrogenated elastomeric block copolymer resin.

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## SPECIFICATION

COMPOSITION OF A POLYSTYRENE RESIN, AND A PRECOMPOUNDED POLYMER SYSTEM  
COMPRISING A POLYOLEFIN AND A SELECTIVELY HYDROGENATED BLOCK  
COPOLYMER OF A VINYL AROMATIC COMPOUND AND AN OLEFINIC ELASTOMER

- 5 This invention relates to novel resin compositions and more particularly, to polymer compositions comprising a polystyrene resin, a precompounded blend of an olefinic resin and a hydrogenated elastomeric block copolymer of a vinyl aromatic compound and an olefinic elastomer, alone, or in further combination with a polystyrene resin and, optionally, a hydrogenated elastomeric block copolymer of a vinyl aromatic compound and an olefinic elastomer. 5
- 10 *Background of the Invention:* The brittleness and lack of impact strength of parts molded from polystyrene resins is a matter of common knowledge and experience. These problems have been overcome in the art by blending rubber into the polystyrene resins, or by forming resins in which polystyrene is grafted onto a rubbery backbone of, e.g., styrene/butadiene random copolymer. Unfortunately, such high impact polystyrene weathers poorly and is unsuitable for out-of-doors 10 applications. 15
- 15 Many manufacturers of high impact polystyrenes have been trying to make them from saturated, e.g., selectively hydrogenated rubbers. In such rubbers, the olefinic unsaturation has been reduced, but the aromatic unsaturation is largely unaffected. These approaches have involved, e.g., an inter-polymerization route which is the technique normally used to produce grafted polystyrenebutadiene 20 backbone resins. To do this, polybutadiene is dissolved in styrene monomer and after about a 7—8% styrene conversion, a phase inversion takes place in which the continuous phase polybutadiene in styrene monomer becomes the dispersed phase under strong stirring. A type of micelle in a polystyrene + styrene monomer phase is formed, the "micelles" looking like droplets. In this way, emulsified rubber particles grafted and partly cross-linked are formed, of which about 2/3 rds is polystyrene occlusion and 25 about 1/3 rd is rubber. This is to say that with a rubber loading of, typically, 10% by weight, the volume percent of rubber, in the form of particles is 30—40%. This particular phenomenon causes a great improvement in impact resistance, e.g., 0.4 ft.lbs./inch of notch in the Izod test rises to 2.5 ft.lbs./in. notch. Unfortunately, however, there is a high reduction in stiffness E from 31,000 to 18,000 and in tensile yield strength, of from 530 to 195 kgf/cm<sup>2</sup>. Also flowability is strongly impaired by the great 30 volume fraction of "non-flowing" rubber particles. In any event, the backbone is unsaturated and this causes poor resistance to attack by oxygen, ozone, heat and ultraviolet light. 30
- 35 A number of workers in this art have also tried to use the so-called EPDM rubbers, e.g., ethylene-propylene diene terpolymers to toughen styrene resins by the technique mentioned above. A difficulty with this is to find useful main chain and grafting reaction conditions. The saturated rubber doesn't contain enough reaction sites for proper grafting and cross-linking. This causes the particles to become large (10—20) and weak. During extrusion and injection molding these particles can easily be disrupted by the shear forces involved during melt flow, resulting in a rather dull surface appearance. 35
- 40 U.S. Patent 3,810,957 (Lunk), has disclosed blends of selectively hydrogenated block copolymers and polystyrene. This blending, e.g., by milling, extruding or Banbury mixing of a poly-styrene resin with a selectively hydrogenated poly(mono vinyl aromatic hydrocarbon)-poly(conjugated diene)-poly 40 (mono vinyl aromatic hydrocarbon) block copolymer produces high impact thermoplastic molding compositions which have greatly improved weathering resistance. The disclosures of the Lunk patent is incorporated herein by reference. Unfortunately, such compositions do produce molded articles which give delamination problems due to the large amounts of saturated rubber needed to obtain reasonable 45 impact levels. 45
- 50 In applicants' copending application, U.S. Serial No. 747,327, filed December 3, 1976, incorporated herein by reference, a major improvement is disclosed in providing high impact strength combinations of polyphenylene ether resins and styrene resins. The improvement comprises adding to the combination a precompounded easily dispersible polymer system, e.g., a polyolefin combined with a rubbery block copolymer, and an additional amount of a rubbery block copolymer. 50
- 55 It has now been discovered that polystyrene resins per se can be remarkably improved in terms of impact strength and processing improvement by intimately admixing them with a precompounded easily dispersible polymer system and, if desired, an additional amount of a hydrogenated block copolymer. The resulting compositions show no tendency to delaminate. They also have a high heat distortion 55 temperature; high gloss; high strength in tension, high stiffness; high creep resistance; high ultra-violet resistance; high aging resistance; high heat resistance during processing; and good flowability.
- 60 It is believed that the surprising efficiency of the system is attributable to the special features of system (b). System (b) consists of a precompounded mixture of a selectively hydrogenated vinyl aromatic-olefin-vinyl aromatic block copolymer and an olefinic resin, e.g., polyethylene, polypropylene and ethylene-propylene copolymers, at a ratio of 20/80 to 80/20, by weight. In any case, dispersibility in component (b) can be further improved by adding a polystyrene, and especially homopolymers of styrene, as a dispersing aid in an amount of up to 100 parts by weight of resinous components, and up to about 10% by weight of other dispersing aids, such as hydrocarbon resins can also be included. 60

The new compositions may also be reinforced, e.g., with fibrous glass, and rendered flame retardant with flame retardant additives to extend their field of use in molded products.

*Description of the Invention:* according to the present invention, there are provided high impact strength thermoplastic compositions comprising an intimate blend of:

- 5 (a) a polystyrene resin; and  
 (b) a precompounded composition comprising from 80 to 20 parts by weight of an olefinic resin comprising poly-ethylene or a poly- $\alpha$ -olefin resin, alone or in further combination with a minor, effective amount of a polystyrene resin and correspondingly from 20 to 80 parts by weight of a selectively hydrogenated linear, sequential or radial teleblock copolymer of a vinyl aromatic com-

10 pound (A)<sub>n</sub> and (A)'<sub>n</sub> and an olefinic elastomer (B), of the A—B—A; A—(B—A—B)<sub>n</sub>—A;

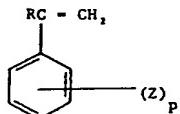
(A(BA)<sub>n</sub>B; (A)<sub>n</sub>B; B(A)<sub>n</sub>; or B[(AB)<sub>n</sub>B]<sub>4</sub> type, wherein n is an integer of 1 to 10; and, optionally.

(c) a selectively hydrogenated elastomeric block copolymer of one of the types set forth in (b).

Preferred compositions will be those in which component (a) comprises from 99 to 60 parts by weight and component (b) comprises from 1 to 40 parts by weight and component (c) comprises from 0 to 20 parts by weight of the total weight of components (a), (b) and (c). In particularly preferred compositions, component (b) comprises from 80 to 20 parts by weight and component (c) from 20 to 80 parts by weight of the total weight of (b) and (c).

With respect to component (a), as is disclosed in the above-mentioned Lunk patent, the polystyrene resins most suitable are polymers of vinyl aromatic hydrocarbons prepared by zene series and include

20 the polymers of styrene and ring-substituted styrene wherein the aromatic nucleus is substituted with one or more alkyl groups preferably containing from 1 to 4 carbon atoms such as methyl or ethyl or with a halogen group such as a chloro group. Examples of such monomers are styrene, vinyl toluene, vinyl xylene, vinyl ethyl benzene, and divinyl benzene. Suitable monomers also include chain-substituted styrenes such as alpha-methyl styrene. Preferably, these polymers have an intrinsic viscosity of from 0 to 25 1.5, especially in the range of 0.6 to 1.0 dl./g., as determined using a 0.25 g./100 ml. solution in toluene at 30°C. The polystyrene resins most preferred are those having at least 25% by weight polymer units derived from vinyl aromatic monomer having the formula:



30 wherein R is hydrogen, alkyl of 1 to 4 carbon atoms or halogen; Z is a member selected from the class consisting of vinyl, hydrogen, or alkyl of from 1 to 4 carbon atoms; and p is from 1 to 5. The preferred polystyrene resins for purposes of this invention are homopolymers.

With respect to component (b) and (c) the hydrogenated block copolymers are made by means known in the art and they are commercially available.

Prior to hydrogenation, the end blocks of these copolymers comprise homopolymers or copolymers 35 preferably prepared from alkenyl aromatic hydrocarbons and particularly vinyl aromatic hydrocarbons wherein the aromatic moiety may be either monocyclic or polycyclic. Typical monomers include styrene, alpha methyl styrene, vinyl xylene, ethyl vinyl xylene and vinyl naphthalene, or mixtures thereof. The end blocks (A) and (A)', may be the same or different. They are preferably selected from styrene,  $\alpha$ -methyl styrene vinyl toluene, vinyl xylene, and vinyl naphthalene, especially styrene. The 40 center block (B) may be derived from, for example, butadiene, isoprene, 1,3-pentadiene, and 2,3-dimethyl butadiene, and it may have a linear, sequential or teleradial structure.

The selectively hydrogenated linear block copolymers are described in U.S. Patent 3,333,024, which is incorporated herein by reference, and also in the above-mentioned Lunk Patent.

The ratio of the copolymers and the average molecular weights can vary broadly although the 45 molecular weight of center block should be greater than that of the combined terminal blocks. It is preferred to form terminal blocks A having average molecular weights of 2,000 to 100,000 and center block B, e.g., a hydrogenated polybutadiene block with an average molecular weight of 25,000 to 1,000,000. Still more preferably, the terminal blocks have average molecular weights of 8,000 to 60,000 while the hydrogenated polybutadiene polymer blocks has an average molecular weight between 50,000 50 and 300,000. The terminal blocks will preferably comprise 2 to 60% by weight, or more, preferably, 15 to 40% by weight, of the total block polymer. The preferred copolymers will be those formed from a copolymer having a hydrogenated/saturated polybutadiene center block wherein 5 to 55%, or more, preferably, 30 to 50% of the butadiene carbon atoms, are vinyl side chains.

The hydrogenated copolymers will have the average unsaturation reduced to less than 20% of the 55 original value. It is preferred to have the unsaturation of the center block B reduced to 10% or less, preferably, 5% of its original value.

The block copolymers are formed by techniques well known to those skilled in the art.

Hydrogenation may be conducted utilizing a variety of hydrogenation catalysts such as nickel or kieselguhr, Raney nickel, copper chromite, molybdenum sulfide and finely divided platinum or other 60 noble metals on a low surface area carrier.

Hydrogenation may be conducted at any desired temperature or pressure, from atmospheric to 300 psig, the usual range being between 100 and 1,000 psig at temperatures from 75°F. to 600°F. for times between 0.1 and 24 hours, preferably, from 0.2 to 8 hours.

- 5 Hydrogenated block copolymers such as Kraton G—6500, Kraton G—6521, Kraton G—1650 and Kraton G—1652 from Shell Chemical Company, Polymers Division, have been found useable according to the present invention. Kraton G—1650 is preferred. Also useable are the so-called hydrogenated Solprene of Phillips, especially the product designated Solprene-512.

- 10 The radial teleblock copolymers of which the Solprene are typical examples can be characterized as having at least three polymer branches with each branch of the radial block polymer comprising terminal non-elastomeric segments, e.g. (A) and (A') as defined hereinabove. The branches of the radial block polymer contain a terminal non-elastomeric segment attached to an elastomeric polymer segment, e.g. (B) as defined above. These are described in U.S. Patent 3,753,936 (Marrs) and in U.S. Patent 3,281,383 (Zelinski) both of which are incorporated herein by reference, and they are selectively hydrogenated by procedures known per se. In any event, the term "selective hydrogenation" is used herein to contemplate polymers in which the elastomeric blocks (B) have been hydrogenated, but the non-elastomeric blocks (A) and (A') have been left unhydrogenated, i.e., aromatic.

15 As is mentioned above, other additives may be present in the compositions, such as pigments, e.g., titanium dioxide.

- 20 With respect to component (b), a variety of polyolefins can be used with the block copolymer to form the premix. In general, it is preferred to use polyethylene or a poly  $\alpha$ -olefin or a copolymer of  $\alpha$ -olefins, the  $\alpha$ -olefin having from 3 to 8 carbon atoms. These can be made by known procedures and are readily available from a number of sources. Especially preferred are polyethylene or polypropylene and their copolymers and block copolymers, e.g., ethylene-propylene copolymer.

- 25 The amount of elastomeric block copolymer, and polyolefins and polystyrene dispersing agent, if used, combined, added to the styrene resin will vary from 1 to 40% by weight of the composition.

- 30 Of course, other additives may be present in the compositions, such as plasticizers, pigments, flame retardants, and the like, in amounts varying between about 1 and 100 parts by weight of the total resinous components (a), (b) and (c) in the composition. The above-stated ranges for amounts of the polystyrene resin (a), the precompounded blend of polyolefin and the hydrogenated elastomeric block copolymer resin (c), if present, is based solely upon such resinous components in the polymer blend and excludes other additives.

- 35 Among the features of this invention are reinforced compositions containing reinforcing amounts of reinforcements, such as powders, whiskers, fibers or platelets of metals, e.g., aluminum, bronze, iron or nickel, and non-metals, e.g., carbon filaments, acicular  $\text{CaSiO}_3$ , asbestos,  $\text{TiO}_2$ , titanate whiskers, and glass flakes. Such reinforcements will be present in an amount of, e.g., 2 to 90% by weight, preferably 10 to 60% by weight. Especially preferred as a reinforcement is fibrous glass.

- 40 The method of forming the polymer composition is non critical, so long as component (b) is precompounded. Any prior art blending technique is generally suitable. The preferred method comprises blending the polymers and any additives, such as reinforcements in powder, granular and filamentous form — as the case may be — extruding the blend and chopping into pellets suitable for molding to shape by means conventionally used to mold normally solid thermoplastic compositions.

*Descriptions of the Preferred Embodiments:* The following examples are set forth as further description of the invention, but are not to be construed as limiting the invention thereto.

- 45 The formulations are produced by a general procedure comprising mechanically blending component (b) into test pieces in a reciprocating screw injection molding machine at about 220°C. (cylinder) and 60°C (mold). To make component (b), the block copolymer and the olefinic resin are masterbatched by precompounding at 204°C. (400°F.) in a twin screw WP or in an adequate rubber processing machine first. The physical tests are carried out by the following procedures: Izod impact strength on 0.32 cm (1/8") notched specimens; falling dart impact tests on 0.32 cm disc specimens; tensile strength and stiffness on ASTM type I bars, drawing rate 0.5 cm./min.; E modulus with an extensiometer on ASTM type I bars, drawing rate of 0.5 cm./min., flow length at 240°C. and 0.3 cm. thickness at constant injection rate and pressure; heat distortion temperature at 18.7 kg/cm<sup>2</sup> (260 psi); and apparent melt viscosity at 1500 sec.<sup>-1</sup> and 282°C. (540°F.).

## EXAMPLES 1 - 4

The following formulations are prepared, molded and tested:

TABLE 1.

Compositions of Styrene Resin and Premix of Hydrogenated Block Copolymer and Polyolefin

Example	1A*	1	2	3	4
<u>Composition (parts by weight)</u>					
d	Styrene Homopolymer <sup>a</sup>	85	90	80	70
	Hydrogenated Styrene-butadiene-styrene block copolymer <sup>b</sup>	—	2.5	3.0	7.5
	Ethylene propylene copolymer <sup>c</sup>	—	2.5	5.0	7.5
	Styrene homopolymer <sup>a</sup>	—	5.0	10.0	15
<u>Properties</u>					
Heat Distortion temp., °C.					
Melt viscosity, poise					
Izod impact, kg/cm (ft.lbs/in.) notch					
Falling dart impact, kg.-m.					
Tensile yield strength, kg.-m.					
E modulus kgf./cm <sup>2</sup>					
Surface appearance					

\* Control

<sup>a</sup> Hoechst N 7000 high heat crystal

<sup>b</sup> Shell Chemical Kraton G 1650

<sup>c</sup> BA-616 Hüls Chemicals Co.

d Premix

The compositions prepared with precompounded resins in accordance with this invention are seen to retain their properties over a wide range of rubber contents and to provide excellent impact resistance even at low block copolymer contents.

TABLE 2 - Composition of Styrene Resin; and Premix of Hydrogenated Block Copolymer and Polyolefin  
 EXAMPLES 5 - 14

Example	5	6	7	8	9	10	11	12	13	14
Composition (parts by weight)										
Styrene homopolymer	85	75	65	80	70	60	75	65	55	45
Hydrogenated styrene-butadiene-styrene block copolymer b	2.5	5.0	7.5	2.5	5	7.5	2.5	5.0	7.5	10
Ethylene propylene copolymer c	2.5	5.0	7.5	2.5	5	7.5	2.5	5.0	7.5	10
Styrene homopolymer a	5	10	15	5	10	10	10	15	15	15
Hydrogenated styrene-butadiene-styrene block copolymer b	5	5	5	10	10	10	15	15	15	15
Properties										
Heat distortion temp., °C.	92	91	90	91	89	89	90	89	87	88
Melt viscosity, poise	1,760	1,840	1,920	1,820	1,860	1,900	1,975	1,990	2,080	2,150
Izod impact, kg/cm notch	7.62	9.25	12.0	10.9	13.9	19.6	15.8	23.1	28.8	34.3
Falling dart impact, kg-m	1.4	1.8	3.1	2.7	3.5	4.3	4.1	4.6	5.1	6.4
Tensile yield strength, kgf./cm <sup>2</sup>	410	375	335	385	370	310	390	315	290	230
E modulus kgf./cm <sup>2</sup>	26,800	24,200	23,200	25,300	23,100	21,900	22,700	20,200	18,300	17,000
Surface appearance	high	high	high	high	med.	high	med.	med.	med.	med.

a Hoechst N 7000 high heat crystal

b Shell Chemical Kraton G 1650

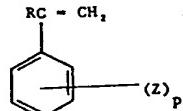
c BA-616 Hüls Chemical Co.

d Premix

The foregoing data demonstrate that high impact polystyrene can be obtained according to this invention with excellent retention of all other important properties.

### CLAIMS

1. A high impact strength thermoplastic composition comprising an intimate blend of:  
 5 (a) a polystyrene resin; and  
 (b) a precompounded composition comprising from 80 to 20 parts by weight of an olefinic resin comprising polyethylene or a poly- $\alpha$ -olefin resin, alone or in further combination with a minor, effective amount of a polystyrene resin, and correspondingly from 20 to 80 parts by weight of a selectively hydrogenated elastomeric linear, sequential or radial teleblock copolymer of a polymerized vinyl aromatic compound (A)<sub>n</sub> and (A)<sup>1</sup> and an olefinic elastomer (B), of the A—B—A'; A—(B—A—B)<sub>n</sub>—A: 10 A(BA)<sub>n</sub>B; (A)<sub>n</sub>B; B(A)<sub>n</sub>; or B[(AB)<sub>n</sub>B]<sub>4</sub> type, wherein n is an integer of from 1 to 10; and optionally  
 15 (c) a selectively hydrogenated elastomeric copolymer of one of the types set forth in (b).  
 2. A composition as defined in claim 1 wherein component (a) comprises from 20 to 60 parts by weight and component (b) comprise from 1—40 parts by weight and component (c) comprises from 0 to 20 parts by weight of the total weight of components (a), (b) and (c).  
 3. A composition as defined in claim 1 wherein component (b) comprises from 80 to 20 parts by weight and component (c) from 20 to 80 parts by weight of the total weight of (b) and (c).  
 4. A composition as defined in any preceding claim wherein component (a) is a polystyrene resin having at least 25% of the polymer units derived from a vinyl aromatic compound of the formula:



wherein R is hydrogen, alkyl of from 1 to 4 carbon atoms or halogen; Z is hydrogen, alkyl of from 1 to 4 carbon atoms or vinyl; and p is an integer of from 1 to 5.

5. A composition as defined in claim 4 wherein the polystyrene resin is a styrene homopolymer resin.  
 25 6. A composition as defined in any preceding claim wherein, in components (b) and (c), vinyl aromatic compounds (A) and (A)<sup>1</sup> are selected from styrene,  $\alpha$ -methyl styrene, vinyl toluene, vinyl xylene and vinyl naphthalene and elastomer (B) is selected from polymerized butadiene, isoprene, 1,3-pentadiene or 2,3-dimethylbutadiene.  
 30 7. A composition as defined in claim 6 wherein, in components (b) and (c), (A)<sub>n</sub> is a poly-styrene block and (A)<sup>1</sup> is a poly-styrene block.  
 8. A composition as defined in any preceding claim wherein, in components (b) and (c), terminal blocks (A)<sub>n</sub> and (A)<sup>1</sup> have molecular weights of 2,000 to 100,000 respectively, and center block (B) has a molecular weight of from 25,000 to 1,000,000.  
 35 9. A composition as defined in any preceding claim wherein, in component (b), said olefinic resin is polyethylene, polypropylene, or an ethylenepropylene copolymer.  
 10. A composition as defined in claim 1 wherein, in component (b), the polystyrene resin comprises a styrene homopolymer.  
 11. A composition as defined in claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 14.